

On the Boltzmann Equation of Thermal Transport for Interacting Phonons and Electrons

Original

On the Boltzmann Equation of Thermal Transport for Interacting Phonons and Electrons / Sparavigna, Amelia Carolina. -
In: MECHANICS, MATERIALS SCIENCE & ENGINEERING JOURNAL. - ISSN 2412-5954. - 2016:5(2016), pp. 1-13.
[10.13140/RG.2.1.2824.0885]

Availability:

This version is available at: 11583/2646088 since: 2016-08-04T18:32:57Z

Publisher:

Magnolithe

Published

DOI:10.13140/RG.2.1.2824.0885

Terms of use:

openAccess

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

On the Boltzmann Equation of Thermal Transport for Interacting Phonons and Electrons

Amelia Carolina Sparavigna¹

¹ – Department of Applied Science and Technology, Politecnico di Torino, Torino, Italy



DOI 10.13140/RG.2.1.2824.0885

Keywords: Boltzmann Equation, thermal conductivity, phonons and electrons.

ABSTRACT. The thermal transport in a solid can be determined by means of the Boltzmann equations regarding its distributions of phonons and electrons, when the solid is subjected to a thermal gradient. After solving the coupled equations, the related thermal conductivities can be obtained. Here we show how to determine the coupled equations for phonons and electrons.

Introduction. In some previous papers we have considered the thermal transport in a solid when just phonons are present [1-6]. Phonons are the quantization of the vibrations of the ions in crystals. They are the quanta which are carrying the thermal energy in the dielectric solids. Since the phonons are interacting among them and with the crystal defects and boundaries, a finite thermal conductivity is observed. Here, we will consider the presence in the solid of both phonons and electrons, subjected to a thermal gradient. The electrons we consider are those which can freely move in the crystal. In fact, these electrons can give rise to several phenomena connected to charge transport: these phenomena will be the subject of a future paper. Here we concentrate just on the effect of a thermal gradient and on the interaction of electrons with phonons and how it can be described by the Boltzmann equation, aiming to introduce the subject to students of engineering colleges.

As shown in [7-9], the interaction among phonons, in three phonons scattering processes for instance, is coming from the Lagrangian of the lattice. In the case that in the solid there are electrons which can support an energy/charge conductivity, these particles, when moving in the solid, are interacting with the ions of the lattice. The use of a pseudopotential [10] allows us to consider the conducting electrons as electrons described by means of a plane waves basis. In this manner we can analyse the transport with an approach based on a perturbative interaction with phonons, neglecting electron-electron interaction and the scattering of electrons with lattice defects. As we have seen for phonons, we can solve the Boltzmann equation for these electrons and determine their contribution to the thermal conductivity. However, the electron-phonon interaction is also influencing the phonon transport, and therefore the phonon thermal conductivity is changed too.

The Boltzmann equation for phonons in a thermal gradient. A thermal gradient in a solid is exciting electrons and phonons which are present in the crystal; they are gaining energy which are transferring, that is conducting, from one end of the solid to the other, moving from the hotter to the coldest side. In metals, both electrons and phonons are playing a relevant role in the thermal conduction, whereas in dielectrics, only phonons are involved. To find the thermal resistance and then the thermal conductivity of the solid, we need to describe several interactions among phonons, electrons, those of phonons with electrons and of phonons and electrons with defects and impurities of the crystals. Moreover the scattering with the boundaries of the crystal have to be considered too.

The problem of evaluating the thermal conductivity in solids is therefore quite complex. It can be solved, from a microscopic point of view [11], using the relaxation time approximation [5,6,11-18], using some variational [19-21] or iterative methods [1-4], or the Green functions [22,23]. The methods based on relaxation time approximations and on variational and iterative methods are based on the Boltzmann equation, whereas the approach with the Green functions is based on quantum statistics. Here we consider the approach based on the Boltzmann equation.

Let us start from phonons. To derive the Boltzmann equation we need that a distribution function $n_{\mathbf{q}p}(\mathbf{r}, t)$ exists concerning the phonon state (\mathbf{q}, p) about position \mathbf{r} , at time t . The state is described by the wave vector \mathbf{q} and by its polarization p . If a thermal gradient ∇T exists, which is changing the temperature $T = T(\mathbf{r})$ in the sample, we will have a diffusion process in the distribution. In this case we can write:

$$\left. \frac{\partial n_{\mathbf{q}p}}{\partial t} \right|_{\text{diff}} = -k_B T \mathbf{v}_p(\mathbf{q}) \cdot \nabla T \frac{\partial n_{\mathbf{q}p}}{\partial T} \quad (1)$$

In (1), $\mathbf{v}_p(\mathbf{q})$ is the group velocity of phonon (\mathbf{q}, p) . Let us observe that the phonon distribution $n_{\mathbf{q}p}$ is depending on space through the temperature $T = T(\mathbf{r})$.

The scattering processes will give a change of the phonon distribution. In the case of a stationary condition, we must have:

$$-k_B T \mathbf{v}_p(\mathbf{q}) \cdot \nabla T \frac{\partial n_{\mathbf{q}p}}{\partial T} + \left. \frac{\partial n_{\mathbf{q}p}}{\partial t} \right|_{\text{scatt}} = 0 \quad (2)$$

This is the general form of the Boltzmann equation [9, 24]. It is an integral-differential equation. A way to solve this equation is in its linearization, considering only the deviation from equilibrium $n_{\mathbf{q}p} - n_{\mathbf{q}p}^0$, being $n_{\mathbf{q}p}^0$ the equilibrium distribution.

The simplest case of scattering we can discuss is that of an elastic scattering. The phonon process is $(\mathbf{q}, p) \rightarrow (\mathbf{q}', p')$, conserving the energy. In this process, we have a transition from the phonon state (\mathbf{q}, p) to the state (\mathbf{q}', p') . The relative probability of a transition in the unit of time is:

$$P_{\mathbf{q}p}^{\mathbf{q}'p'} = n_{\mathbf{q}p} (n_{\mathbf{q}'p'} + 1) Z_{\mathbf{q}p}^{\mathbf{q}'p'} \quad (3)$$

In (3), $Z_{\mathbf{q}p}^{\mathbf{q}'p'}$ is the intrinsic probability, that is the probability not depending on the occupation of phonon states (\mathbf{q}, p) and (\mathbf{q}', p') . Therefore, the probability of the transition from (\mathbf{q}', p') to (\mathbf{q}, p) is:

$$P_{\mathbf{q}'p'}^{\mathbf{q}p} = n_{\mathbf{q}'p'} (n_{\mathbf{q}p} + 1) Z_{\mathbf{q}'p'}^{\mathbf{q}p} \quad (4)$$

where

$$Z_{\mathbf{q}'p'}^{\mathbf{qp}} = Z_{\mathbf{qp}}^{\mathbf{q}'p'} \quad (5)$$

Because the variation of the phonon distribution is equal to the probability of having a scattering per unit of time, we have:

$$\left. \frac{\partial n_{\mathbf{qp}}}{\partial t} \right|_{\text{scatt}} = \sum_{\mathbf{q}'p'} (P_{\mathbf{q}'p'}^{\mathbf{qp}} - P_{\mathbf{qp}}^{\mathbf{q}'p'}) = \sum_{\mathbf{q}'p'} [n_{\mathbf{q}'p'}(n_{\mathbf{qp}} + 1) - n_{\mathbf{qp}}(n_{\mathbf{q}'p'} + 1)] Z_{\mathbf{qp}}^{\mathbf{q}'p'} \quad (6)$$

After simplifying and linearizing we find:

$$\left. \frac{\partial n_{\mathbf{qp}}}{\partial t} \right|_{\text{scatt}} = \sum_{\mathbf{q}'p'} [(n_{\mathbf{q}'p'} - n_{\mathbf{q}'p'}^0) - (n_{\mathbf{qp}} - n_{\mathbf{qp}}^0)] Z_{\mathbf{qp}}^{\mathbf{q}'p'} \quad (7)$$

In (7), $n_{\mathbf{qp}}^0 = n_{\mathbf{q}'p'}^0$, because $n_{\mathbf{qp}}^0$ is depending just on energy and that in an elastic process:

$$\hbar \omega(\mathbf{q}, p) = \hbar \omega(\mathbf{q}', p') \quad (8)$$

The linearized Boltzmann equation turns out to be:

$$-k_B T \mathbf{v}_p(\mathbf{q}) \cdot \nabla T \frac{\partial n_{\mathbf{qp}}^0}{\partial T} = \sum_{\mathbf{q}'p'} [(n_{\mathbf{qp}} - n_{\mathbf{qp}}^0) - (n_{\mathbf{q}'p'} - n_{\mathbf{q}'p'}^0)] Z_{\mathbf{qp}}^{\mathbf{q}'p'} \quad (9)$$

In (9), to evaluate $\partial n_{\mathbf{qp}} / \partial T$ we used only the equilibrium distribution $n_{\mathbf{qp}}^0$.

In the general case, to obtain the linearized Boltzmann equation we use the deviation from equilibrium $\Psi_{\mathbf{qp}}$ in the following manner:

$$n_{\mathbf{qp}} = n_{\mathbf{qp}}^0 - \Psi_{\mathbf{qp}} \frac{\partial n_{\mathbf{qp}}^0}{\partial(\hbar \omega_{\mathbf{qp}})} \quad (10')$$

Let us assume $x = \hbar \omega_{\mathbf{qp}} / k_B T$, where k_B is the Boltzmann constant. From (10') we have:

$$\frac{\partial n_{\mathbf{qp}}^0}{\partial(\hbar\omega_{\mathbf{qp}})} = \frac{\partial n_{\mathbf{qp}}^0}{\partial x} \frac{\partial x}{\partial(\hbar\omega_{\mathbf{qp}})} = \frac{1}{k_B T} \frac{\partial}{\partial x} \left\{ \frac{1}{e^x - 1} \right\} = \frac{1}{k_B T} n_{\mathbf{qp}}^0 (n_{\mathbf{qp}}^0 + 1) \quad (10'')$$

Therefore:

$$n_{\mathbf{qp}} = n_{\mathbf{qp}}^0 - \Psi_{\mathbf{qp}} \frac{\partial n_{\mathbf{qp}}^0}{\partial(\hbar\omega_{\mathbf{qp}})} = n_{\mathbf{qp}}^0 + \frac{\Psi_{\mathbf{qp}}}{k_B T} n_{\mathbf{qp}}^0 (n_{\mathbf{qp}}^0 + 1) \quad (10''')$$

For the elastic scattering:

$$-k_B T \mathbf{v}_p(\mathbf{q}) \cdot \nabla T \frac{\partial n_{\mathbf{qp}}^0}{\partial T} = \sum_{\mathbf{q}'p'} [\Psi_{\mathbf{qp}} n_{\mathbf{qp}}^0 (n_{\mathbf{qp}}^0 + 1) - \Psi_{\mathbf{q}'p'} n_{\mathbf{q}'p'}^0 (n_{\mathbf{q}'p'}^0 + 1)] Z_{\mathbf{qp}}^{\mathbf{q}'p'} \quad (11)$$

That is:

$$k_B T \mathbf{v}_p(\mathbf{q}) \cdot \nabla T \frac{\partial n_{\mathbf{qp}}^0}{\partial T} = \sum_{\mathbf{q}'p'} [\Psi_{\mathbf{q}'p'} - \Psi_{\mathbf{qp}}] Q_{\mathbf{qp}}^{\mathbf{q}'p'} \quad (12)$$

$$Q_{\mathbf{qp}}^{\mathbf{q}'p'} = n_{\mathbf{qp}}^0 (n_{\mathbf{qp}}^0 + 1) Z_{\mathbf{qp}}^{\mathbf{q}'p'} \quad (13)$$

With this formalism, in the case that we have three-phonon processes, the linearized Boltzmann equation is:

$$\begin{aligned} k_B T \mathbf{v}_p(\mathbf{q}) \cdot \nabla T \frac{\partial n_{\mathbf{qp}}^0}{\partial T} = & \sum_{\mathbf{q}'p'} \sum_{\mathbf{q}''p''} Q_{\mathbf{qp},\mathbf{q}'p'}^{\mathbf{q}''p''} [\Psi_{\mathbf{q}''p''} - \Psi_{\mathbf{q}'p'} - \Psi_{\mathbf{qp}}] + \\ & + \frac{1}{2} \sum_{\mathbf{q}'p'} \sum_{\mathbf{q}''p''} Q_{\mathbf{qp}}^{\mathbf{q}'p',\mathbf{q}''p''} [\Psi_{\mathbf{q}''p''} + \Psi_{\mathbf{q}'p'} - \Psi_{\mathbf{qp}}] \end{aligned} \quad (14)$$

In the linearized Boltzmann equation, we have the additions on phonons \mathbf{q}' and \mathbf{q}'' of the Brillouin Zone. However, sums can be converted into integrals:

$$\sum_{\mathbf{q}'} \rightarrow \frac{\Omega}{(2\pi)^3} \int d^3 \mathbf{q}' = \frac{\Omega}{(2\pi)^3} \left(\frac{2\pi\sqrt{2}}{h_1} \right) \int_0^{2\pi} d\theta' \int_0^{H(\theta')} \eta' d\eta' \int_{-M(\theta',\eta')}^{M(\theta',\eta')} d\zeta' \quad (15)$$

In (15), $\Omega = NV$ is the volume of the crystal, made of N lattice cells each with volume V . H and M are the functions describing the boundary of the Brillouin Zone, and h_1 is the nearest neighbor site distance [1].

Once obtained the deviation of the distribution function, the Boltzmann equation is solved and the thermal current \mathbf{U} can be calculated as:

$$\mathbf{U} = \frac{1}{\Omega} \sum_{\mathbf{q}p} \hbar \omega_{\mathbf{q}p} \mathbf{v}_{\mathbf{q}p} n_{\mathbf{q}p} = -\frac{1}{\Omega} \sum_{\mathbf{q}p} \hbar \omega_{\mathbf{q}p} \mathbf{v}_{\mathbf{q}p} \frac{\partial n_{\mathbf{q}p}^0}{\partial (\hbar \omega_{\mathbf{q}p})} \Psi_{\mathbf{q}p} \quad (16)$$

In a Cartesian frame of reference having unit vectors \mathbf{u}_i , current \mathbf{U} is represented by:

$$U_j = -\sum_i \kappa_{ji} \frac{\partial T}{\partial x_i} \quad (17)$$

In (17) κ_{ij} is a term of the thermal conductivity tensor, which is diagonal ($\kappa_{xx} = \kappa_{yy} = \kappa_{zz} = \kappa$).

Besides the phonon-phonon interaction, a phonon can be subjected to a scattering coming from the lattice defects and from electrons [1-6].

The Boltzmann Equation for electrons Let us use symbol Q when considering a phonon having wave-vector \mathbf{q} , polarization p and frequency $\omega_{\mathbf{q}p}$. And also use simply k for an electron having wave-vector \mathbf{k} , and energy ε_k and spin σ . Supposing a thermal gradient disturbing the distribution of electrons from equilibrium f_k^0 to a distribution f_k , let us assume, as we did for phonons:

$$f_k - f_k^0 = \Phi_k \frac{f_k^0 (1 - f_k^0)}{k_B T} \quad (18)$$

The equilibrium distribution f_k^0 is that of Fermi-Dirac, where each energy level is occupied by an electron. In it, we have the Fermi energy ε_F . This threshold is obtained by the distribution f_k^0 which becomes a step function of energy when the Kelvin temperature is null. For non-null temperature:

$$f_k^0 = \frac{1}{1 + e^{(\varepsilon - \varepsilon_F)/k_B T}} \quad (19)$$

Let us have free electrons described by \mathbf{k} . At null temperature, the energy levels would be occupied till the radius k_F so that:

$$\varepsilon_F = \frac{\hbar^2}{2m_e} k_F^2 \quad (20)$$

In (20), m_e is the mass of the electron. For a non-null temperature, some electrons have $|\mathbf{k}| > k_F$ and then they can be above the Fermi energy.

In (18), the deviation from equilibrium $f_k - f_k^0$, coming from the presence of a thermal gradient, is considered with the same approach we followed to solve the Boltzmann equation for phonons (see Eqs. (10')-(10'')).

Let $\Pi_{k\mathbf{q}}^{k'}$, $\Pi_k^{k'\mathbf{q}}$ be the intrinsic probability of an electron-phonon scattering of an electron \mathbf{k} interacting with a phonon \mathbf{q} as shown in the following scheme (Figure 1). After the scattering, the electron has momentum \mathbf{k}' , because it had gained a phonon or lost it [9].

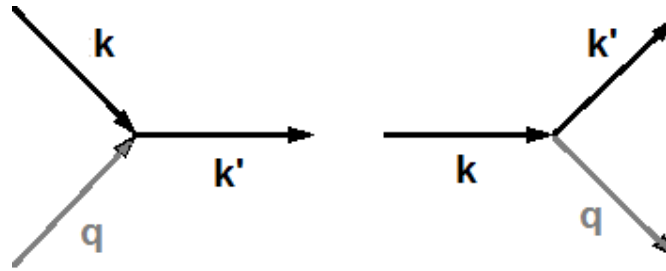


Figure 1: An electron changes its momentum after it has gained or lost a phonon.

Of course, as in the case of phonons, we can have processes involving the \mathbf{g} vectors of the reciprocal lattice. The electron-phonon scatterings are adding new contributions in the scattering term of the Boltzmann equation for phonons. For instance, if we consider the case when just three-phonon scattering processes are present, to them we have to add the scattering from electrons:

$$\left(\frac{\partial n_Q}{\partial t} \right)_{scatt} = \sum_{\mathbf{k}\sigma} \sum_{\mathbf{k}'\sigma'} P_{kQ}^{k'} \delta_{\sigma\sigma'} (\Phi_{k'} - \Psi_Q - \Phi_k) + \sum_{\mathbf{k}\sigma} \sum_{\mathbf{k}'\sigma'} P_k^{k'Q} \delta_{\sigma\sigma'} (\Phi_{k'} + \Psi_Q - \Phi_k) \\ + \frac{1}{2} \sum_{Q'Q''} Q_Q^{Q'Q''} (\Psi_{Q''} - \Psi_Q + \Psi_{Q'}) + \sum_{Q'Q''} Q_Q^{Q''} (\Psi_{Q''} - \Psi_Q - \Psi_{Q'}) \quad (21')$$

Then, the linearized Boltzmann equation is:

$$k_B T \mathbf{v}_p(\mathbf{q}) \cdot \nabla T \frac{\partial n_{qp}^0}{\partial T} = \sum_{\mathbf{k}\sigma} \sum_{\mathbf{k}'\sigma'} P_{kQ}^{k'} \delta_{\sigma\sigma'} (\Phi_{k'} - \Psi_Q - \Phi_k) + \sum_{\mathbf{k}\sigma} \sum_{\mathbf{k}'\sigma'} P_k^{k'Q} \delta_{\sigma\sigma'} (\Phi_{k'} + \Psi_Q - \Phi_k) \\ + \frac{1}{2} \sum_{Q'Q''} Q_Q^{Q'Q''} (\Psi_{Q''} - \Psi_Q + \Psi_{Q'}) + \sum_{Q'Q''} Q_Q^{Q''} (\Psi_{Q''} - \Psi_Q - \Psi_{Q'}) \quad (21'')$$

Symbol σ is indicating electronic spin. Delta $\delta_{\sigma\sigma'}$ is considering the conservation of electronic spin. Probabilities are given by the following expressions:

$$P_{k\mathbf{q}}^{k'} = \Pi_{k\mathbf{q}}^{k'} f_k^0 n_{\mathbf{q}}^0 (1 - f_{k'}^0) \quad (22)$$

$$P_k^{k'\mathbf{q}} = \Pi_k^{k'\mathbf{q}} f_k^0 (1 + n_{\mathbf{q}}^0) (1 - f_{k'}^0) \quad (23)$$

In metals, electrons too are contributing to the thermal transport. In the Boltzmann equation for electrons, we find the scattering with phonons [9]:

$$\left(\frac{\partial f_k}{\partial t} \right)_{scatt} = - \sum_{Q\mathbf{k}'\sigma'} P_{\mathbf{k}Q}^{k'} \delta_{\sigma\sigma'} (\Phi_k + \Psi_Q - \Phi_{k'}) - \sum_{Q\mathbf{k}'\sigma'} P_{\mathbf{k}}^{k'Q} \delta_{\sigma\sigma'} (\Phi_k - \Psi_Q - \Phi_{k'}) \quad (24')$$

Then, the linearize Boltzmann equation for electrons is:

$$k_B T \mathbf{v}_k \cdot \nabla T \frac{\partial f_k^0}{\partial T} = - \sum_{Q\mathbf{k}'\sigma'} P_{\mathbf{k}Q}^{k'} \delta_{\sigma\sigma'} (\Phi_k + \Psi_Q - \Phi_{k'}) - \sum_{Q\mathbf{k}'\sigma'} P_{\mathbf{k}}^{k'Q} \delta_{\sigma\sigma'} (\Phi_k - \Psi_Q - \Phi_{k'}) \quad (24'')$$

From the theory of electron-phonon scattering [9], the probability $P_{\mathbf{k}Q}^{k'}$ turns out to be:

$$P_{\mathbf{k}Q}^{k'} = \Re(|\mathbf{k}' - \mathbf{k}|) \frac{[\mathbf{e}_{\mathbf{q}p} \cdot (\mathbf{k}' - \mathbf{k})]^2}{\omega_{\mathbf{q}p}} f_{\mathbf{k}}^0 n_{\mathbf{q}}^0 (1 - f_{\mathbf{k}'}^0) \delta(\varepsilon_{\mathbf{k}} + \hbar\omega_{\mathbf{q}p} - \varepsilon_{\mathbf{k}'}) \quad (25)$$

$$P_{\mathbf{k}}^{k'Q} = \Re(|\mathbf{k}' - \mathbf{k}|) \frac{[\mathbf{e}_{\mathbf{q}p} \cdot (\mathbf{k}' - \mathbf{k})]^2}{\omega_{\mathbf{q}p}} f_{\mathbf{k}}^0 (1 + n_{\mathbf{q}}^0) (1 - f_{\mathbf{k}'}^0) \delta(\varepsilon_{\mathbf{k}} - \hbar\omega_{\mathbf{q}} - \varepsilon_{\mathbf{k}'}) \quad (26)$$

In (25) and (26) we find the polarization vectors \mathbf{e} of phonons. The interaction between electron and lattice is described by the function $\Re(\mathbf{k})$. It can be described by means of a pseudopotential for instance.

Let us note that we have to consider the conservation of energy and of the generalized conservation of momentum given by the following expression:

$$\mathbf{k} + \mathbf{q} = \mathbf{k}' + \mathbf{g} ; \mathbf{k} - \mathbf{q} = \mathbf{k}' + \mathbf{g}$$

The coupled Boltzmann linearized equations for phonons and electrons can be solved in an iterative approach for instance. Another question we have to discuss before solving the equation is the description of interaction. This will be shortly analysed in the next section.

Scattering electron-phonon Let us consider the following scheme (Figure 2):

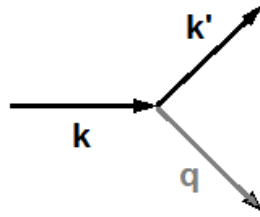


Figure 2: A scattering electron-phonon

In this process we have a phonon having momentum \mathbf{q} and polarization p added to the population n_Q so that population becomes $n_Q + 1$. Then, the initial quantum state is given by $|i\rangle = \psi_k |n_Q\rangle$ and the final quantum state is $|j\rangle = \psi_{k'} |n_Q + 1\rangle$. If we use a pseudopotential approach [24], the electron can be described by plane waves [25-27], so that:

$$\psi_k = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}\cdot\mathbf{r}} ; \psi_{k'} = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{k}'\cdot\mathbf{r}} \quad (27)$$

Let us remember that a pseudopotential is an effective potential used as an approximation for the simplified description of complex systems. It is an attempt to consider the effects of the motion of the core, that is of the non-valence electrons of an atom and of the nucleus with an effective potential, so that the Schrödinger equation contains such effective potential instead of the Coulomb terms for the core electrons. In this manner the valence electrons are described by pseudo-wave functions, in which a plane-wave basis is used.

We can write the scattering as the passage from the initial state $|i\rangle$ to the final state $|f\rangle$ through pseudopotential W [25,26]:

$$\begin{aligned} \langle f | W | i \rangle &= \int \Psi_{k'}^*(\mathbf{r}) \langle n_Q + 1 | W(\mathbf{r}) | n_Q \rangle \Psi_k(\mathbf{r}) d^3x = \langle n_Q + 1 | \int \Psi_{k'}^*(\mathbf{r}) W(\mathbf{r}) \Psi_k(\mathbf{r}) d^3x | n_Q \rangle \\ &= \langle n_Q + 1 | \frac{1}{\Omega} \int e^{-i(\mathbf{k}' - \mathbf{k})\cdot\mathbf{r}} W(\mathbf{r}) d^3x | n_Q \rangle = \langle n_Q + 1 | W_{\mathbf{k}' - \mathbf{k}} | n_Q \rangle \end{aligned} \quad (28)$$

Moreover, we can write [25-27]:

$$W_{\mathbf{k}' - \mathbf{k}} = \frac{NS(\mathbf{k}' - \mathbf{k}) w(\mathbf{k}' - \mathbf{k})}{\varepsilon(\mathbf{k}' - \mathbf{k})} \quad (29)$$

In (29), w is the pseudopotential generated by a single ion which is acting on the electron. N is the number of lattice sites. We find also in (29) the static dielectric constant ε , which can be written as the following function [25-27] (e is the electron charge):

$$\varepsilon_Q = 1 + \frac{4\pi e^2}{Q^2} \frac{m_e k_F}{2\pi^2 \hbar^2} \left[\frac{1 - (Q/2k_F)^2}{(Q/2k_F)} \ln \left| \frac{1 + (Q/2k_F)}{1 - (Q/2k_F)} \right| + 1 \right] \quad (30)$$

Moreover (l is giving the lattice site described by the position vector \mathbf{l}):

$$\begin{aligned} NS(\mathbf{k}' - \mathbf{k}) &= \sum_l e^{-i(\mathbf{k}' - \mathbf{k}) \cdot (\mathbf{l} + \mathbf{u}_l)} \\ &= \sum_l e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{l}} e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{u}_l} = \sum_l e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{l}} [1 - i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{u}_l + \dots] \end{aligned}$$

As usual, the phononic function of the displacement of the lattice site given by the position vector \mathbf{l} is [9,10]:

$$\mathbf{u}_l = i \sqrt{\frac{\hbar}{2mN}} \sum_{\mathbf{q}p} \frac{1}{\sqrt{\omega_{\mathbf{q}p}}} \left[\mathbf{e}_{\mathbf{q}p}^* e^{-i\mathbf{q} \cdot \mathbf{l}} a_{\mathbf{q}p} - \mathbf{e}_{\mathbf{q}p} e^{i\mathbf{q} \cdot \mathbf{l}} a_{\mathbf{q}p}^+ \right] \quad (31)$$

In (31), m is the mass of ions. In this manner we can write the matrix:

$$\langle f | W | i \rangle = \frac{w(\mathbf{k}' - \mathbf{k})}{\varepsilon(\mathbf{k}' - \mathbf{k})} \left\langle n_Q + 1 \left| \sum_l e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{l}} [1 - i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{u}_l] \right| n_Q \right\rangle \quad (32)$$

Then, we can obtain:

$$\begin{aligned} \langle f | W | i \rangle &= \frac{w(\mathbf{k}' - \mathbf{k})}{\varepsilon(\mathbf{k}' - \mathbf{k})} \left\{ \left\langle n_Q + 1 \left| \sum_l e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{l}} \right| n_Q \right\rangle \right. \\ &\quad \left. + \left\langle n_Q + 1 \left| (\mathbf{k}' - \mathbf{k}) \sqrt{\frac{\hbar}{2mN}} \sum_l e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{l}} \sum_{\mathbf{q}p} \frac{1}{\sqrt{\omega_{\mathbf{q}p}}} \left[\mathbf{e}_{\mathbf{q}p}^* e^{-i\mathbf{q} \cdot \mathbf{l}} a_{\mathbf{q}p} - \mathbf{e}_{\mathbf{q}p} e^{i\mathbf{q} \cdot \mathbf{l}} a_{\mathbf{q}p}^+ \right] \right| n_Q \right\rangle \right\} \quad (33) \end{aligned}$$

Of the matrix, just the element having a_Q^+ , which is creating phonon \mathbf{q}, p survives, and then:

$$\langle f | W | i \rangle = - \frac{w(\mathbf{k}' - \mathbf{k})}{\varepsilon(\mathbf{k}' - \mathbf{k})} \sqrt{\frac{\hbar}{2mN}} \frac{\mathbf{e}_{\mathbf{q}p} \cdot (\mathbf{k}' - \mathbf{k})}{\sqrt{\omega_{\mathbf{q}p}}} \sum_l e^{-i(\mathbf{k}' - \mathbf{k}) \cdot \mathbf{l}} e^{i\mathbf{q} \cdot \mathbf{l}} \langle n_Q + 1 | a_{\mathbf{q}p}^+ | n_Q \rangle \quad (34)$$

Since $\sum_l e^{-i(\mathbf{k}' - \mathbf{k} + \mathbf{q}) \cdot \mathbf{l}} = N \delta_{\mathbf{k}' - \mathbf{k} + \mathbf{q}, \mathbf{g}}$ and $\langle n_Q + 1 | a_{\mathbf{q}p}^+ | n_Q \rangle = \sqrt{n_Q + 1}$, we have:

$$\langle f|W|i\rangle = -\frac{w(\mathbf{k}'-\mathbf{k})}{\varepsilon(\mathbf{k}'-\mathbf{k})} N \sqrt{\frac{\hbar}{2mN}} \frac{\mathbf{e}_{\mathbf{qp}} \cdot (\mathbf{k}'-\mathbf{k})}{\sqrt{\omega_{\mathbf{qp}}}} \sqrt{n_Q+1} \quad (35)$$

Of course, we have the generalized conservation of momentum $\mathbf{k}'-\mathbf{k}+\mathbf{q}=\mathbf{g}$. Therefore, the probability for the unit of time is:

$$\begin{aligned} & \frac{2\pi}{\hbar} |\langle f|W|i\rangle|^2 \delta(E_f - E_i) \\ &= \frac{2\pi}{\hbar} \left[\frac{w(\mathbf{k}'-\mathbf{k})}{\varepsilon(\mathbf{k}'-\mathbf{k})} \right]^2 \frac{\hbar N}{2m} \frac{[\mathbf{e}_{\mathbf{qp}} \cdot (\mathbf{k}'-\mathbf{k})]^2}{\omega_{\mathbf{qp}}} (n_Q+1) \delta(\varepsilon_{k'} + \hbar\omega_{\mathbf{qp}} - \varepsilon_k) \end{aligned} \quad (36)$$

The conservation of energy is represented by $\delta(E_f - E_i)$. Eq.36 is the intrinsic probability that an electron can move from \mathbf{k} to \mathbf{k}' . This probability is conditioned by the fact that \mathbf{k} state is occupied and \mathbf{k}' is empty, due to the Pauli exclusion principle. The true probability is then (36) multiplied by $f_k(1-f_{k'})$. Therefore we have:

$$P_k^{k'Q} = \frac{2\pi}{\hbar} \left[\frac{w(\mathbf{k}'-\mathbf{k})}{\varepsilon(\mathbf{k}'-\mathbf{k})} \right]^2 \frac{\hbar N}{2m} \frac{[\mathbf{e}_{\mathbf{qp}} \cdot (\mathbf{k}'-\mathbf{k})]^2}{\omega_{\mathbf{qp}}} f_k(1-f_{k'})(n_Q+1) \delta(\varepsilon_{k'} + \hbar\omega_Q - \varepsilon_k) \quad (37)$$

This is in agreement to (25) if we have:

$$\Re(\mathbf{k}'-\mathbf{k}) = \frac{\pi N}{m} \left[\frac{w(\mathbf{k}'-\mathbf{k})}{\varepsilon(\mathbf{k}'-\mathbf{k})} \right]^2 \quad (38)$$

In the Boltzmann equation we have also to consider the other scattering mechanism shown in the Figure 3. In this case we have to consider $\langle n_Q-1|a_Q|n_Q\rangle$ and generalized conservation $\mathbf{k}+\mathbf{q}=\mathbf{k}'+\mathbf{g}$. In this manner, it is straightforward to obtain $P_{kQ}^{k'}$.

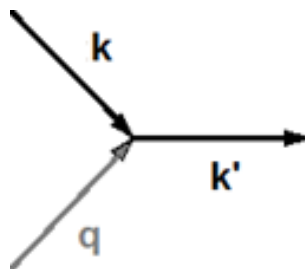


Figure 3: The other scattering electron-phonon process.

Thermal conductivity As given in [28], the thermal current of electrons is the following:

$$\mathbf{U} = \frac{2}{\Omega} \sum_k f_k \mathbf{v}_k (\varepsilon_k - \varepsilon_F) \quad (39)$$

In (39), we find the velocity and energy of electrons. We have also the chemical potential, that we will consider as ε_F . We can follow the same approach used for the phonons so that:

$$\mathbf{U} = \frac{2}{\Omega} \sum_k \mathbf{v}_k (\varepsilon_k - \varepsilon_F) \frac{\partial f_k^0}{\partial \varepsilon_k} \Phi_k \quad (40)$$

In the approach we have shown here, the equilibrium distribution of electrons f^0 is a spherical symmetric function. Then, for the evaluation of the thermal electronic conductivity we can use spherical coordinates k, α, θ . The electronic thermal conductivity is given by [9,28]:

$$\kappa = -\lambda \int_0^\infty \bar{k}^2 d\bar{k} \int_0^\pi \sin(\alpha) d\alpha \int_0^{2\pi} d\theta (\bar{k}^2 - 1) \bar{k} \cos(\alpha) f_k^0 (1 - f_k^0) \phi(\bar{k}, \alpha, \theta) \quad (41)$$

In (41), a reduced momentum \bar{k} and the dimensionless deviation function ϕ had been used so that the dimensional factor turns out to be [29]:

$$\lambda = \frac{k_F^9 \hbar^8 V}{64\pi^2 m_e^5 k_B T^2 e^4 \hbar^2} \sqrt{\frac{3mU_o}{2}} \quad (42)$$

In (42), parameter U_o is linked to the potential used for calculating the lattice thermal conductivity [1, 2].

In a future paper we will explain how to solve iteratively the coupled equations (21'') and (24''). Once the deviation functions of phononic and electronic distributions have been obtained the thermal phononic and the electronic thermal conductivities can be calculated from (16) and (41).

References

- [1] Omini, M., & Sparavigna, A. (1996). Beyond the isotropic-model approximation in the theory of thermal conductivity. *Physical Review B*, 53(14), 9064-9073. DOI: 10.1103/physrevb.53.9064
- [2] Omini, M., & Sparavigna, A. (1997). Heat transport in dielectric solids with diamond structure. *Nuovo Cimento D Serie*, 19, 1537.
- [3] Omini, M., & Sparavigna, A. (1995). An iterative approach to the phonon Boltzmann equation in the theory of thermal conductivity. *Physica B: Condensed Matter*, 212(2), 101-112. DOI: 10.1016/0921-4526(95)00016-3

- [4] Omini, M., & Sparavigna, A. (1997). Effect of phonon scattering by isotope impurities on the thermal conductivity of dielectric solids. *Physica B: Condensed Matter*, 233(2), 230-240. DOI: 10.1016/s0921-4526(97)00296-2
- [5] Sparavigna, A. C. (2016). The Boltzmann equation of phonon thermal transport solved in the relaxation time approximation – I – Theory. *Mechanics, Materials Science & Engineering Journal*, (3), 1-13. DOI: 10.13140/RG.2.1.1001.1923
- [6] Sparavigna, A. C. (2016). The Boltzmann equation of phonon thermal transport solved in the relaxation time approximation – II – Data analysis. *Mechanics, Materials Science & Engineering Journal*, 2016(3), 1-10. DOI: 10.13140/RG.2.1.2026.4724
- [7] Srivastava, G. P. (1990). *The physics of phonons*. CRC Press.
- [8] Kittel, C., & Fong, C. Y. (1963). *Quantum theory of solids* (Vol. 33). New York: Wiley.
- [9] Ziman, J. M. (1960). *Electrons and phonons: the theory of transport phenomena in solids*. Oxford University Press.
- [10] Srivastava, S. K., & March, N. H. (Eds.). (1995). *Condensed Matter - Disordered Solids*. World Scientific.
- [11] Peierls, R. (1935). Quelques propriétés typiques des corps solides. In *Annales de l'institut Henri Poincaré*, 5(3), 177-222.
- [12] Klemens, P. G. (1951). The thermal conductivity of dielectric solids at low temperatures (theoretical). In *Proceedings of the Royal Society of London A: Mathematical, Physical and Engineering Sciences*, 208(1092), 108-133. DOI: 10.1098/rspa.1951.0147
- [13] Klemens, P. G. (1958). Thermal conductivity and lattice vibrational modes. *Solid State Physics*, 7, 1-98. DOI: 10.1016/s0081-1947(08)60551-2
- [14] Callaway, J. (1959). Model for lattice thermal conductivity at low temperatures. *Physical Review*, 113(4), 1046-1051. DOI: 10.1103/physrev.113.1046
- [15] Krumhansl, J. A. (1965). Thermal conductivity of insulating crystals in the presence of normal processes. *Proceedings of the Physical Society*, 85(5), 921-9130. DOI: 10.1088/0370-1328/85/5/310
- [16] Srivastava, G. P. (1976). Calculation of lattice thermal conductivity of Ge from 4 to 900 K. *Philosophical Magazine*, 34(5), 795-809. DOI: 10.1080/14786437608222052
- [17] Srivastava, G. P. (1980). Phonon conductivity of insulators and semiconductors. *Journal of Physics and Chemistry of Solids*, 41(4), 357-368. DOI: 10.1016/0038-1098(80)90461-5
- [18] Parrott, J. E. (1971). Generalization of the Callaway thermal conductivity equation. *Physica Status Solidi (b)*, 48(2), K159-K161. DOI: 10.1002/pssb.2220480266
- [19] Guyer, R. A., & Krumhansl, J. A. (1966). Solution of the linearized phonon Boltzmann equation. *Physical Review*, 148(2), 766-778. DOI: 10.1103/physrev.148.766
- [20] Srivastava, G. P. (1980). Phonon conductivity of insulators and semiconductors. *Journal of Physics and Chemistry of Solids*, 41(4), 357-368. DOI: 10.1016/0038-1098(80)90461-5
- [21] Omini, M., & Sparavigna, A. (1993). Thermal conductivity of rare gas crystals the role of three-phonon processes. *Philosophical Magazine B*, 68(5), 767-785. DOI: 10.1080/13642819308220158
- [22] Jancel, R. (2013). *Foundations of classical and quantum statistical mechanics: International Series of Monographs in Natural Philosophy* (Vol. 19). Elsevier.
- [23] Gurevich, V. L. V. (1986). *Transport in phonon systems*. Amsterdam, North-Holland.
- [24] Mizutani, U. (2001). *Introduction to the Electron Theory of Metals*, Cambridge University Press.

- [25] Barbero, D., & Omini, M. (1984). Vacancy formation volume of sodium, aluminium and argon. *Il Nuovo Cimento D*, 3(3), 533-560. DOI: 10.1007/bf02457768
- [26] Omini, M. (1994). Phonon-phonon interaction and phonon drag in potassium at low temperatures. *Philosophical Magazine B: Physics of Condensed Matter*, 69(6), 1197-1215. DOI: 10.1080/01418639408240189
- [27] Sparavigna, A. C. Appunti di un seminario del Professor Omini sullo pseudopotenziale (unpublished).
- [28] Ziman, J. M. (1975). *I principi della teoria dei solidi*. Tamburini Editore.
- [29] Ponasso, L. & Sparavigna, A. (2001). Determinazione del trasporto termico nei metalli con approccio iterativo all'equazione di Boltzmann. In: LXXXVII Congresso Nazionale Società Italiana di fisica, Milano, Milano, 24-29 Settembre 2001. Page 71.